# Microscopy Investigation on the Fading Mechanism of Electrode Materials


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2017 DOE Vehicle Technologies Program Review
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Project ID#: ES226

# Overview

## Timeline

- Start date: Oct. 1, 2015
- End date: Sept. 30, 2018
- Percent complete:50%

## Budget

- Total project funding: $900k
  - DOE share: 100%
- Funding received in FY 2016: $300k
- Funding for FY17: $255k

## Barriers addressed

- Fading and failure mechanism of electrodes
- High theoretical capacity of electrode materials cannot be fully utilized

## Partners

- Material synthesis group in PNNL
- Lawrence Berkeley National Lab
- Argonne National Lab
- Stanford University
- National Renewable Energy Lab
- GM Research Center
- University of Texas at Austin
- Hydro Quebec
- EnerG2 company
- FEI Company
- Hummingbird Scientific Inc.

# Relevance/Objectives

- Develop *ex-situ*, *in situ* and *operando* HRTEM and associated spectroscopic techniques for rechargeable battery research

- Use *ex-situ*, *in situ* and *operando* HRTEM and in-situ spectroscopic technique to probe the fading mechanism of electrode materials

- Correlation of structural and chemical evolution with battery performance for guiding the designing of new materials

# Milestones

- Intragranular cracking of layer structured cathode and its correlation with battery performance (03/31/2017). Complete.

- Atomic level identification of the behavior of Ni, Mn, Co, and Al in the NCM and NCA when cycled at high voltage and correlate with fading mechanism (06/31/2017). On track

- ETEM studies of the Ni segregation characteristics and its correlation with materials processing temperature (9/30/2017). On track

- Bulk lattice degradation mechanism of NMC and NCA cathode (06/31/2018). On track

- Mass and charge transport study of secondary particle to mitigate intergranular degradation (09/30/2018). On track

# Approach/Strategy

- Using the state-of-the-art aberration corrected S/TEM, EELS, and EDS to probe chemistry and structure of electrode

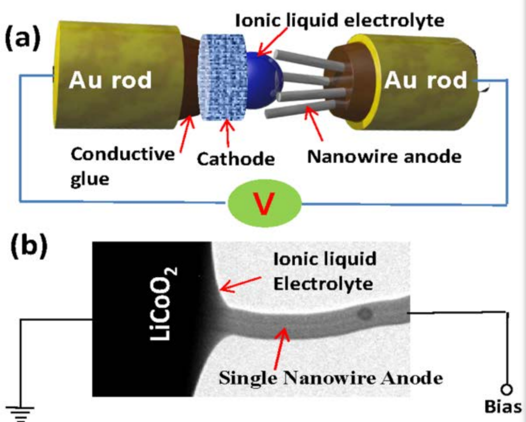
- Extend and enhance the unique ex-situ and in situ S/TEM methods and associated spectroscopic technique for probing the fading mechanism of Li-ion battery under dynamic operating condition

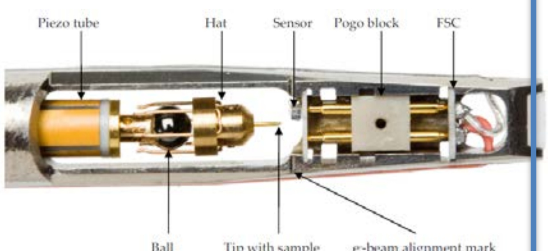
- Establish close collaboration/integration with battery research and development groups to capture the cutting edge questions that facing the battery research/ development

# Technical Accomplishments:

## Developed In-Situ Environmental TEM Enabling the Controlled Gas Environment around the Sample

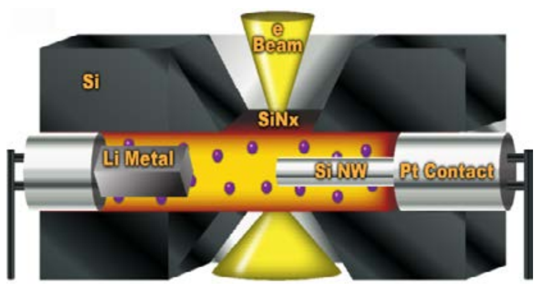
### Open cell in-situ TEM



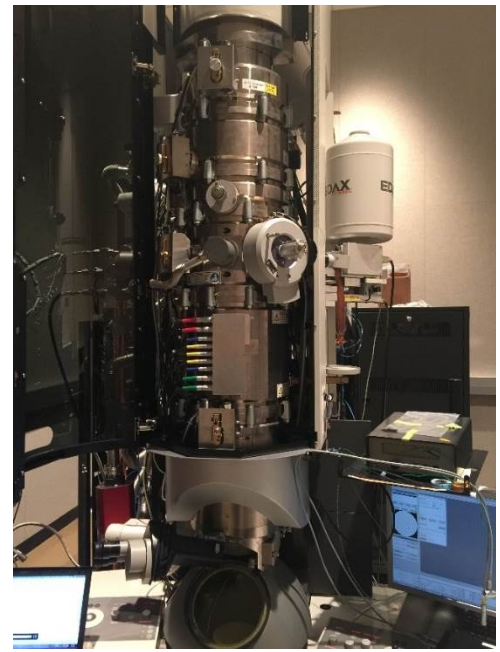

*J. Y. Huang and C. M,. Wang et al, Science, 330(2010)1515*

### Closed cell in-situ TEM




*M. Gu and C. M. Wang et al, Nano Letter, 13 (2013)6106*

### In-Situ Environmental TEM

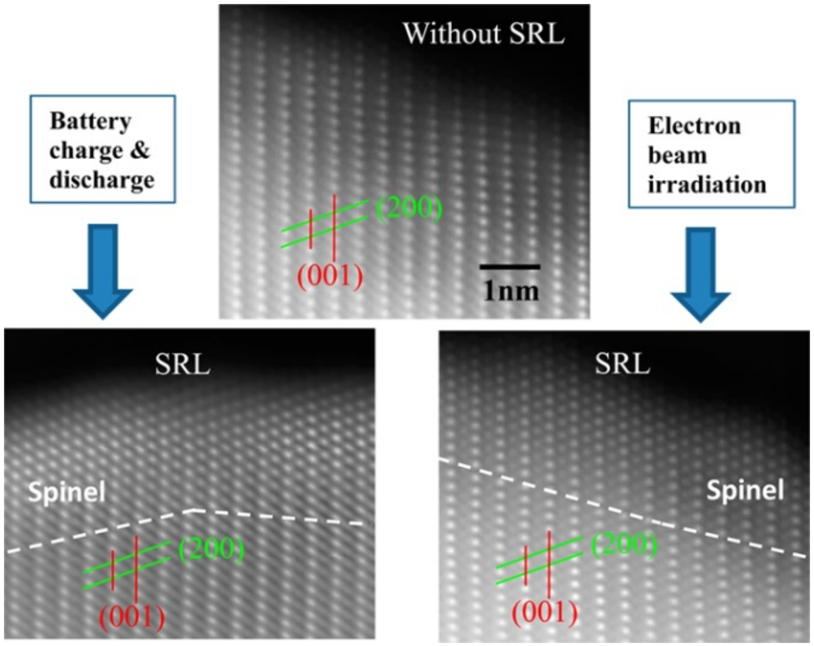


*L. L. Luo and C. M. Wang et al, Nature Nanotechnology, 2017,*
DOI: 10.1038/NNANO.2017.27, *online*

**Towards real battery operating condition**

# Technical Accomplishments:

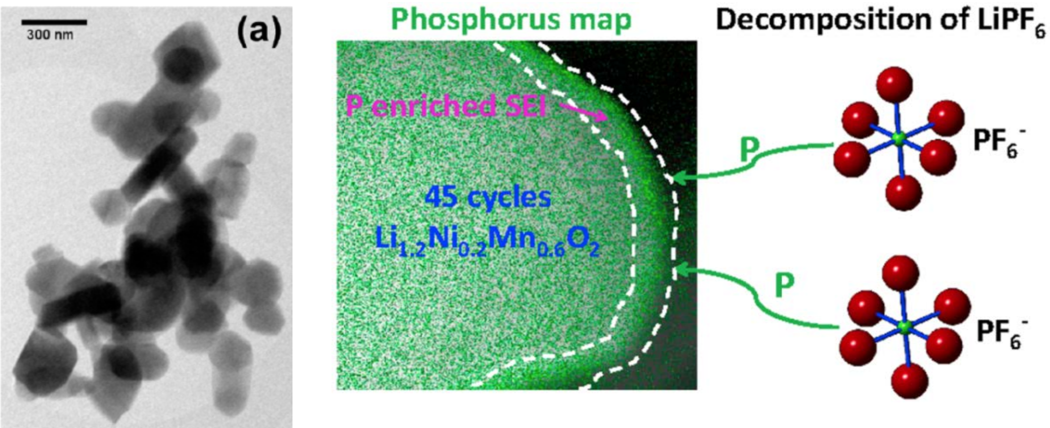
How does the Layer Structured Cathode Fail: Everything Appears to be Associated with Surface Process, a Consequence of Solid-Liquid Interaction

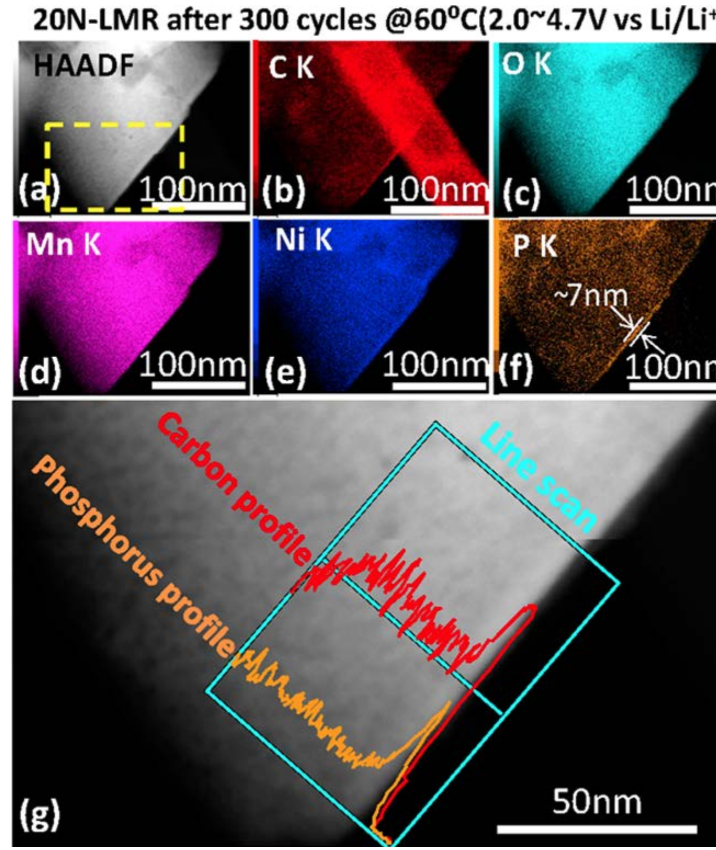



- Surface reconstruction: layer to spinel/rock salt transition
- Migration of transition metal to Li layer
- Mobility of transition metal ions
- Oxygen loss
- Transition metal dissolution/migration/deposition on anode
- Intergranular and intragranular cracking
- Oxygen redox effect
- Coating layer work in someway
- How does it work? Or other consequences following the coating?

# Technical Accomplishments:

Cathode-Electrolyte ($LiPF_6$ in EC-DMC) Interaction Leads to Electrolyte Depletion of Salt




| | Phosphorus Concentration (at. %) | | |
|---|---|---|---|
| | 2.0−4.2 V | 2.0−4.7 V | 3.0−5.0 V |
| 10 cycles, $Li_2MnO_3$ | | 7 ± 1 | |
| 45 cycles, NC-LMR | | 5 ± 1 | |
| 45 cycles, 20N-LMR | | 5 ± 1 | |
| 105 cycles, NCM424 | <1 | 3 ± 1 | |
| 45 cycles, NCA | <1 | 4 ± 1 | |
| 45 cycles, $LiNi_{0.5}Mn_{1.5}O_4$ | | | <1 |

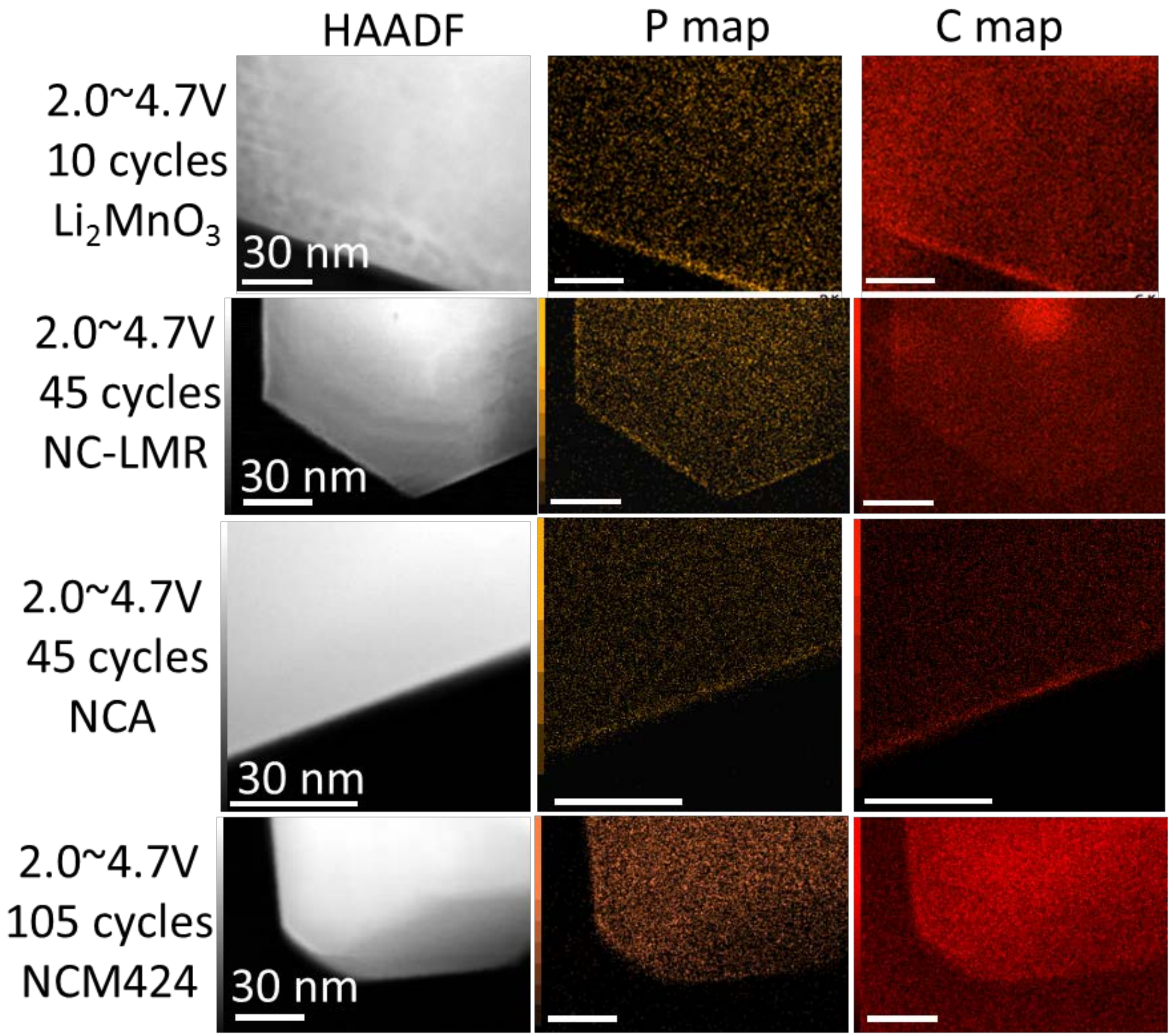
- Structure, voltage, and temperature affect the electrolyte decomposition.
- Spinel phase is more stable than layered structure



*Pengfei Yan and C. M. Wang et al, Nano Letter, 15 (2015)6170*

# Technical Accomplishments:

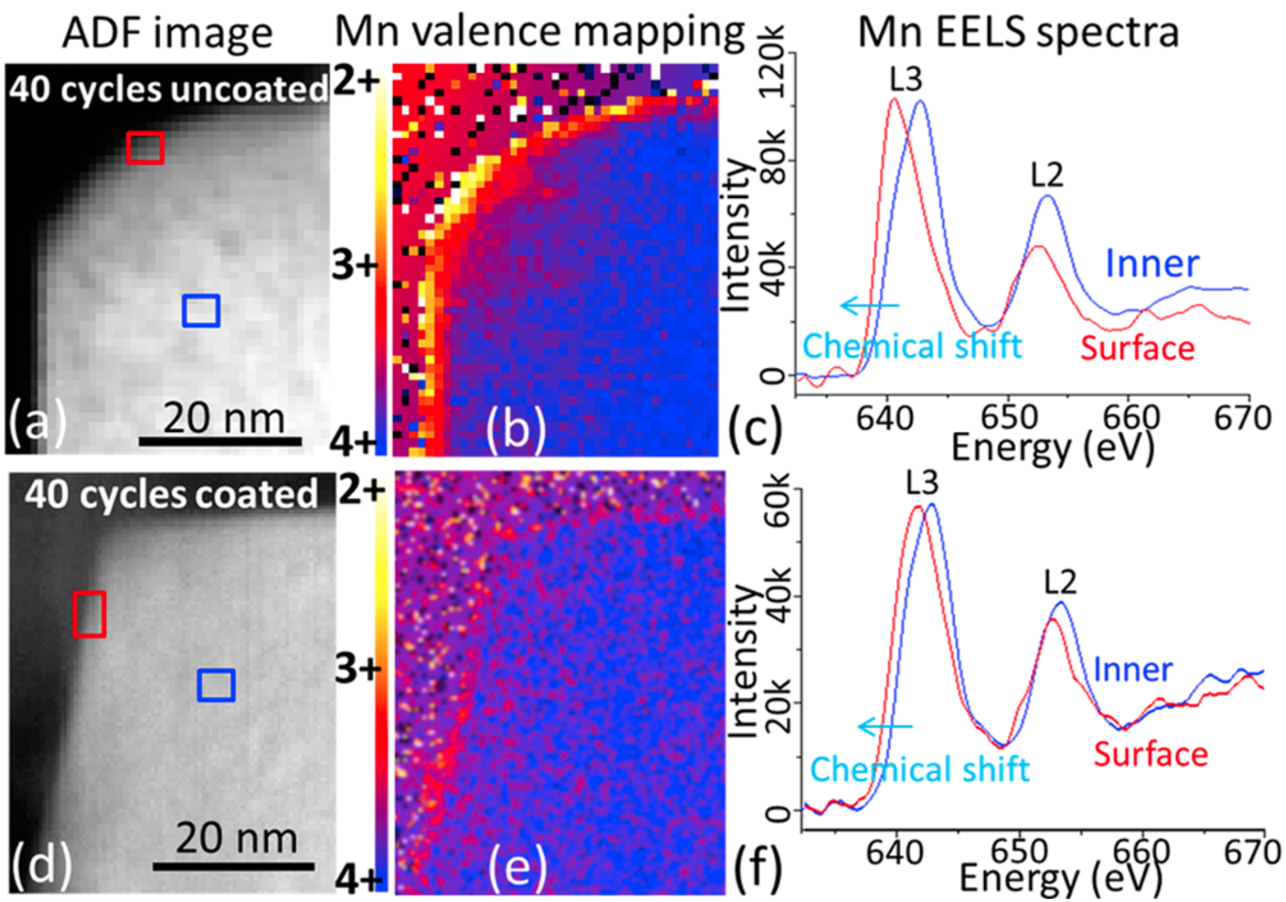
## STEM-EDS Analysis of SEI on Layered Cathode Materials




*Pengfei Yan et al, Chem. Mater., 28, 857(2016)*

# Technical Accomplishments:

## Direct Visualization of How $Al_2O_3$ Coating Affects the Surface Electronic Structure of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$

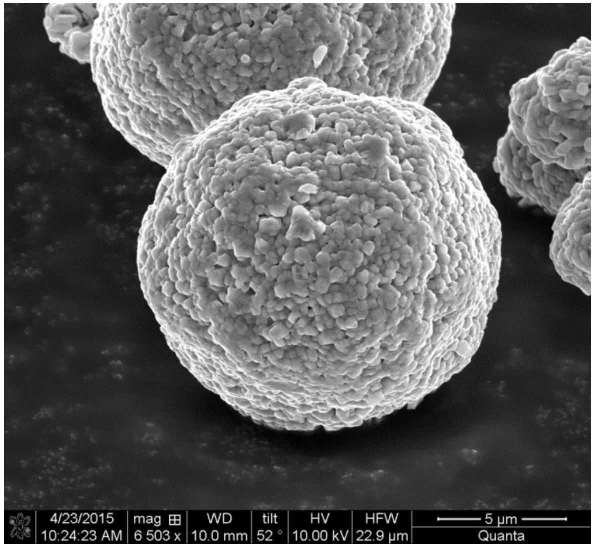


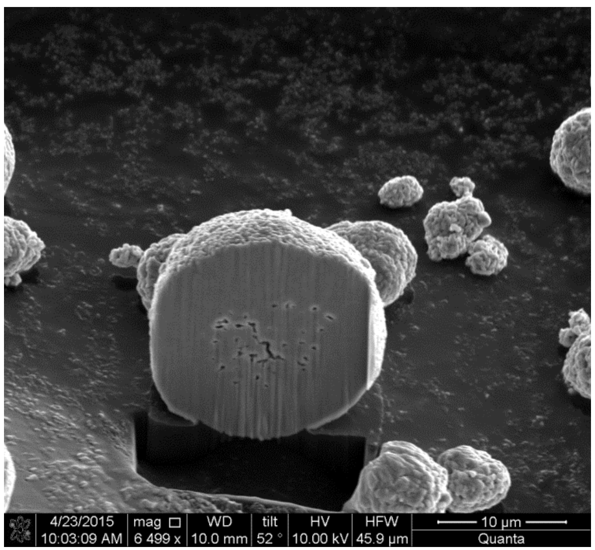

- Use STEM−EELS to map valence of LMR cathode after 40 cycles and study the effect of the $Al_2O_3$ coating layer
- With the $Al_2O_3$ coating, the reduction of Mn is mitigated at the particle surface

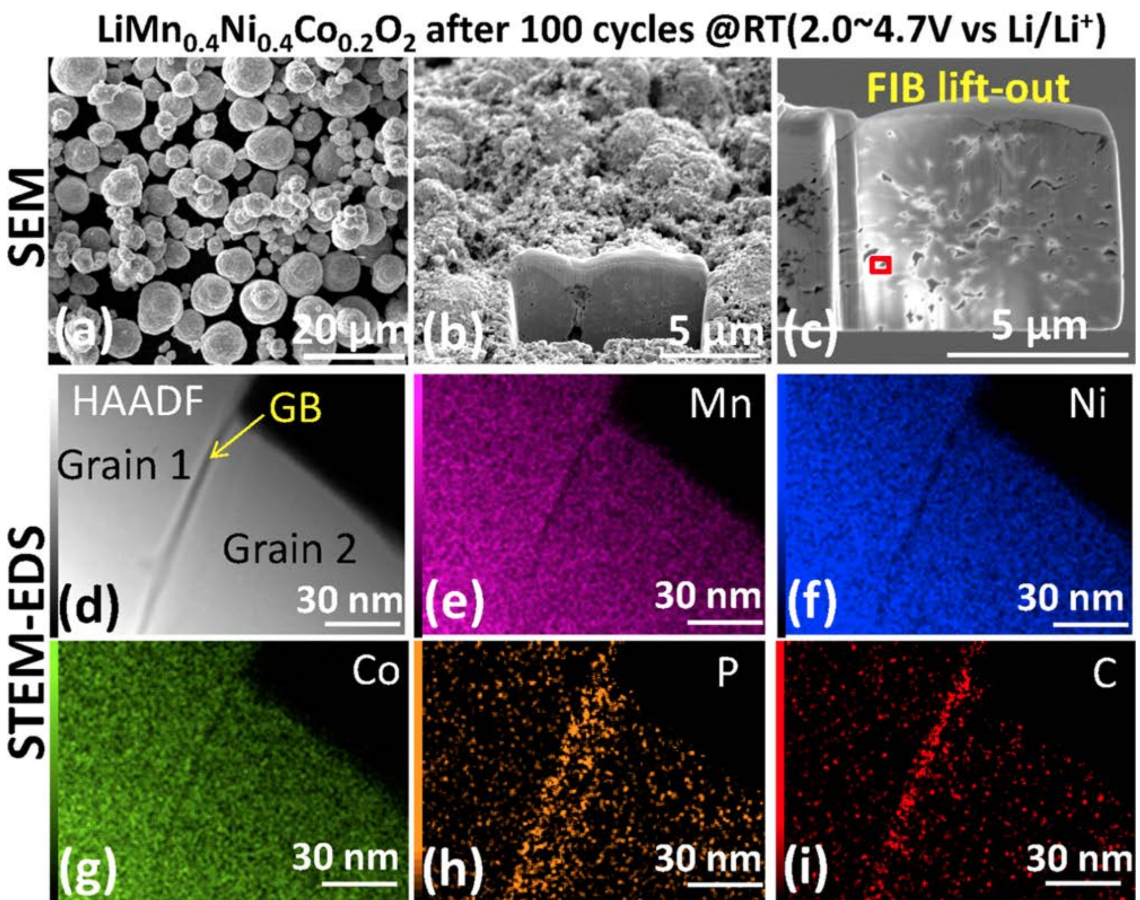
*Pengfei Yan et al, Chem. Mater., 28, 857(2016)*

# Technical Accomplishments:

Penetration of the Electrolyte into the Boundaries of the Large Aggregate of Cathode



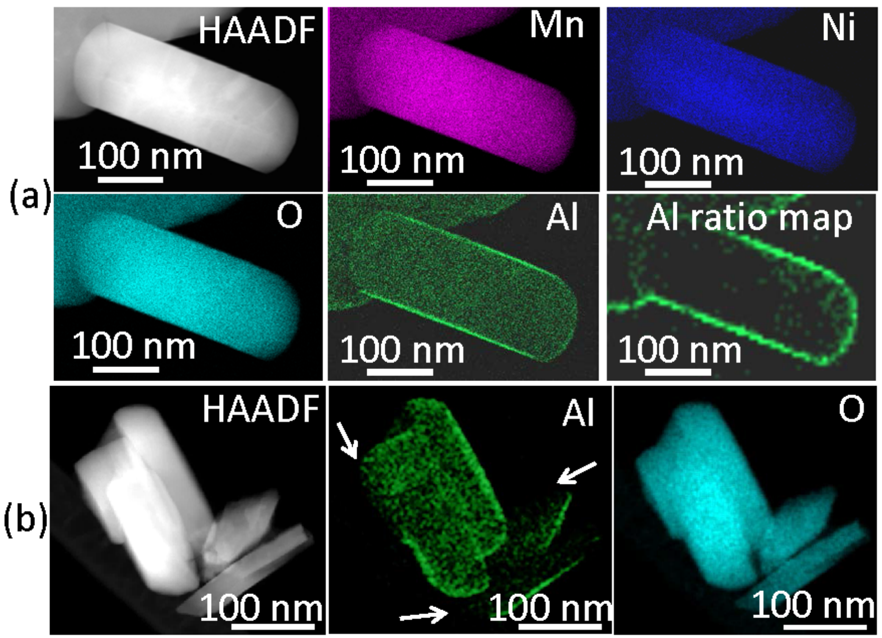



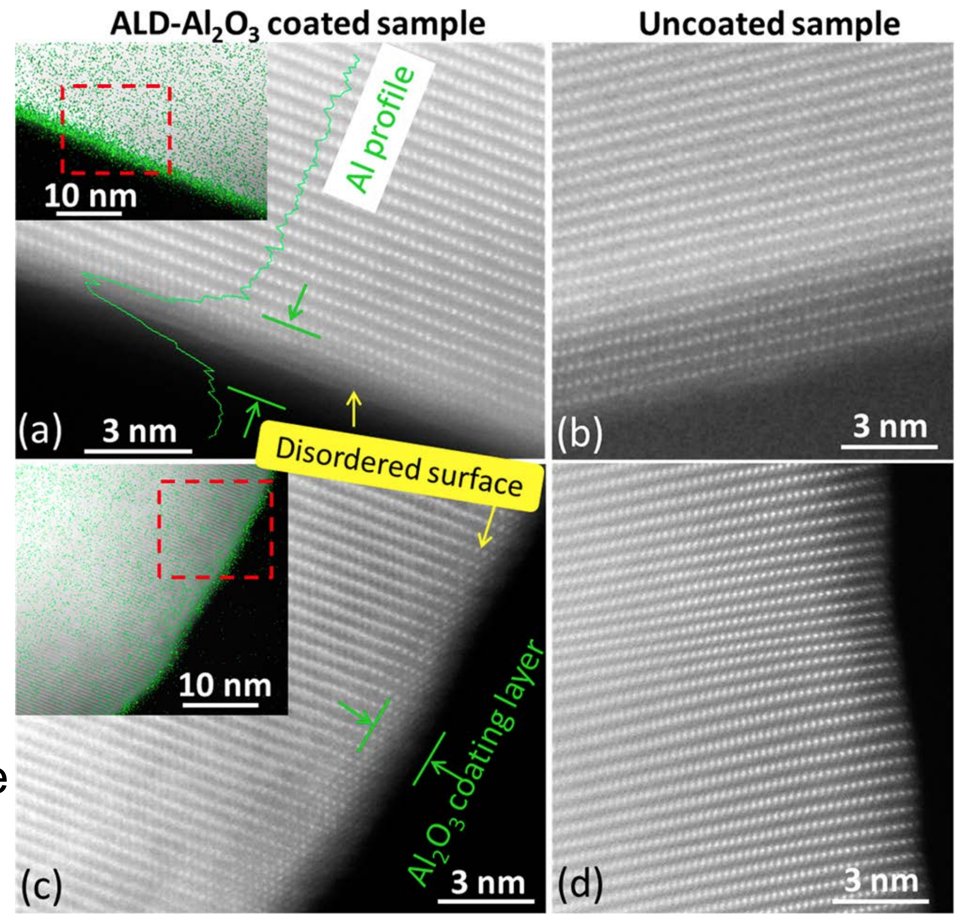




- The boundary between the particle is wetted by the electrolyte species

# Technical Accomplishments:

## Mitigation of Cathode-Electrolyte Reaction by Surface Coating: Chemical and Structural Information of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ Coated with $Al_2O_3$ Using ALD



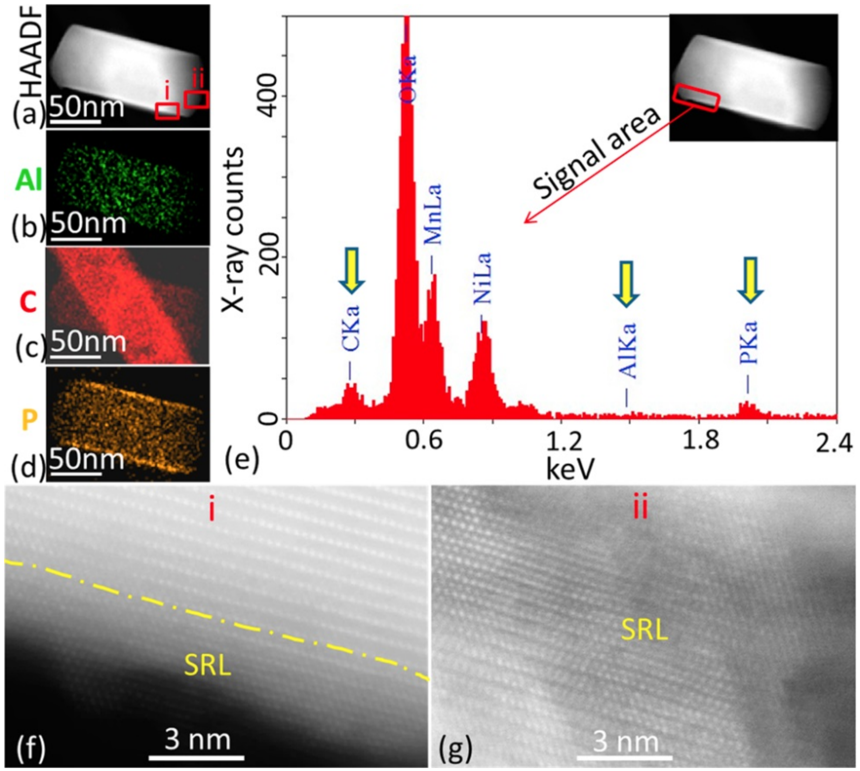



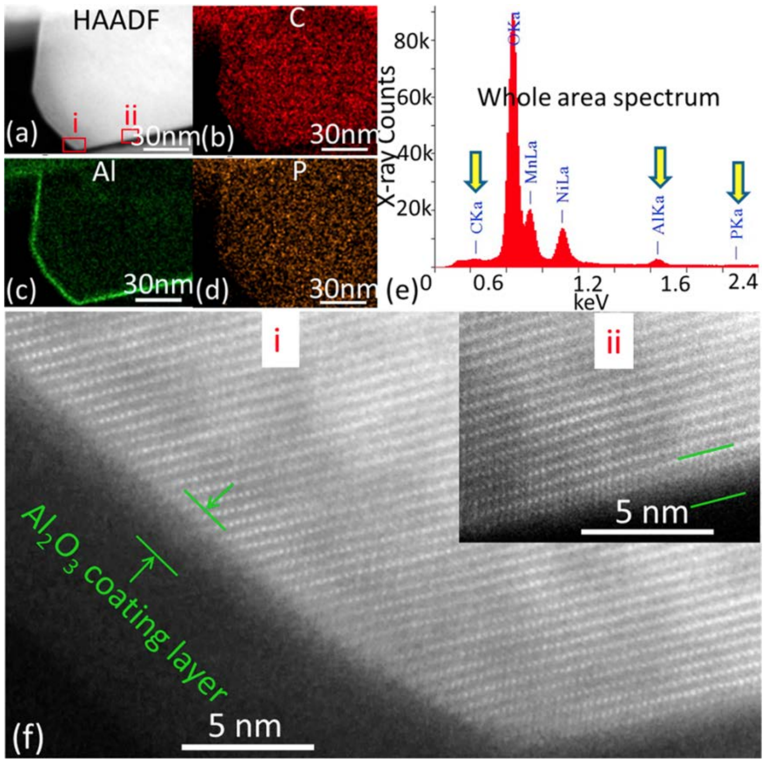

- ALD generally gives uniform coating layer on the particle surface as revealed by the STEM-EDS mapping
- Coating leads to structural modification of the particle surface

*Pengfei Yan et al, Chem. Mater., 28, 857(2016)*

# Technical Accomplishments:

## Direct Visualization of How $Al_2O_3$ Coating Affects the Surface Chemistry and Structure of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$



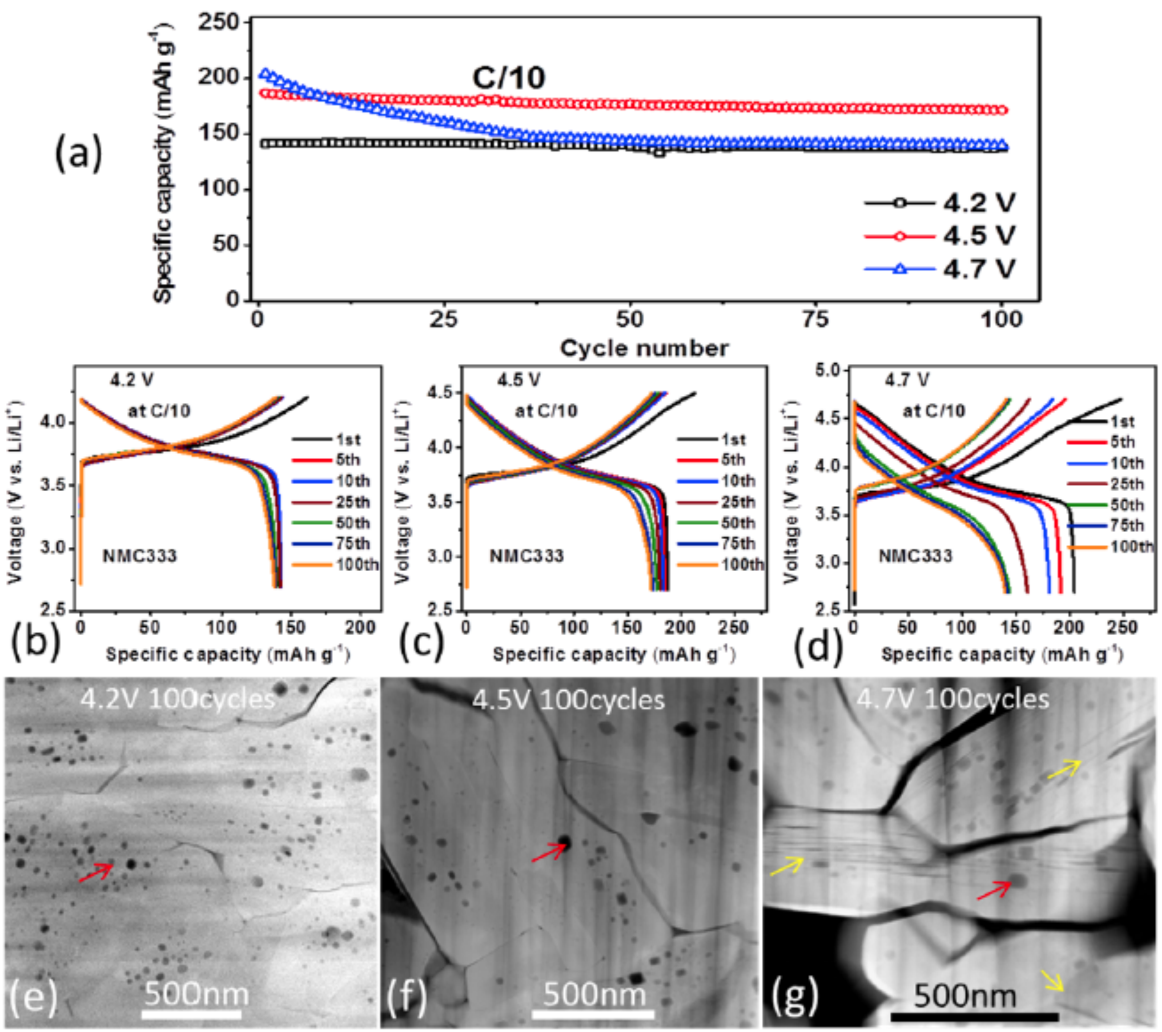

$Al_2O_3$ coating effect:

- Suppress cathode-electrolyte reaction
- Mitigate the surface Mn reduction and dissolution
- Suppress layer to spinel phase transition

*Pengfei Yan et al, Chem. Mater., 28, 857(2016)*

# Technical Accomplishments:

Intergranular Cracking in the Secondary Particle and Intragranular Cracking in the Primary Particles in NMC333

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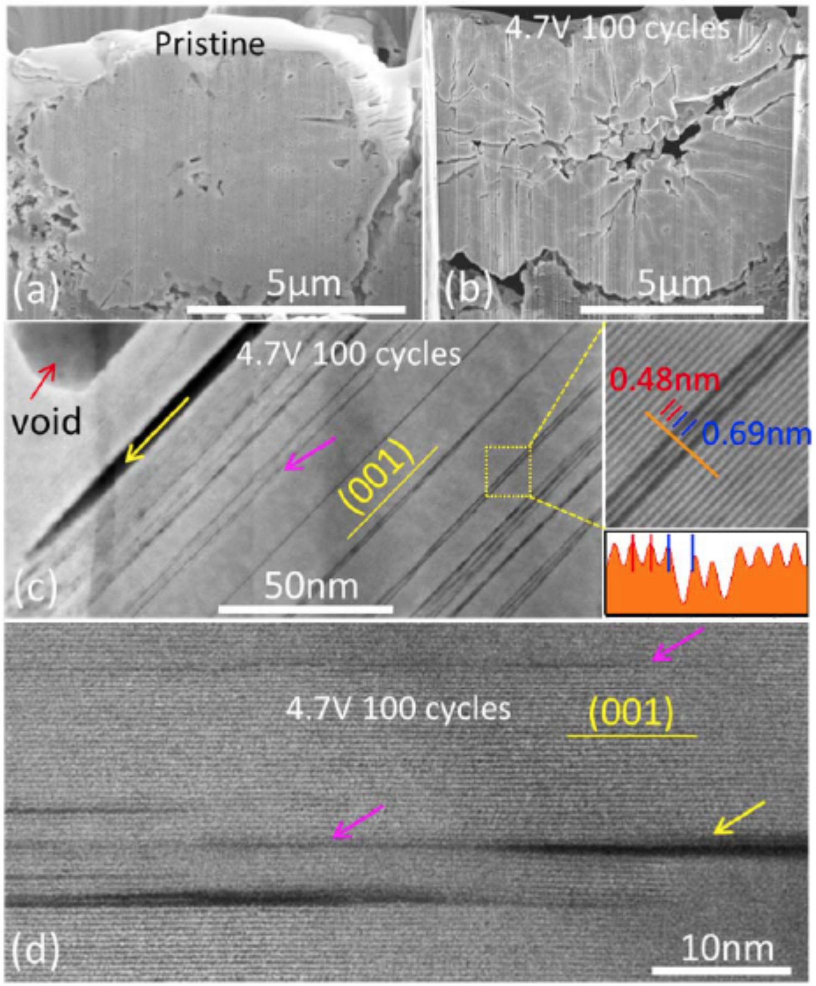
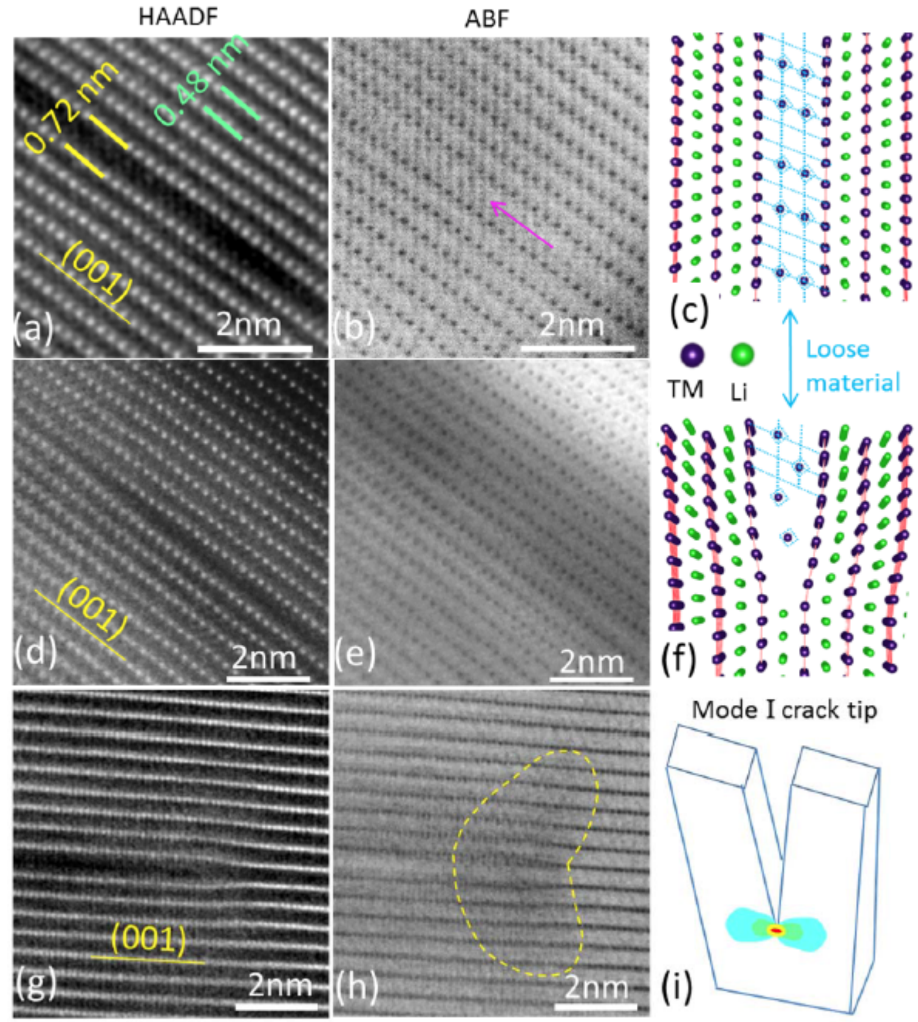
# Technical Accomplishments:

## Atomic Structural Model of the Intragranular Crack in NMC333

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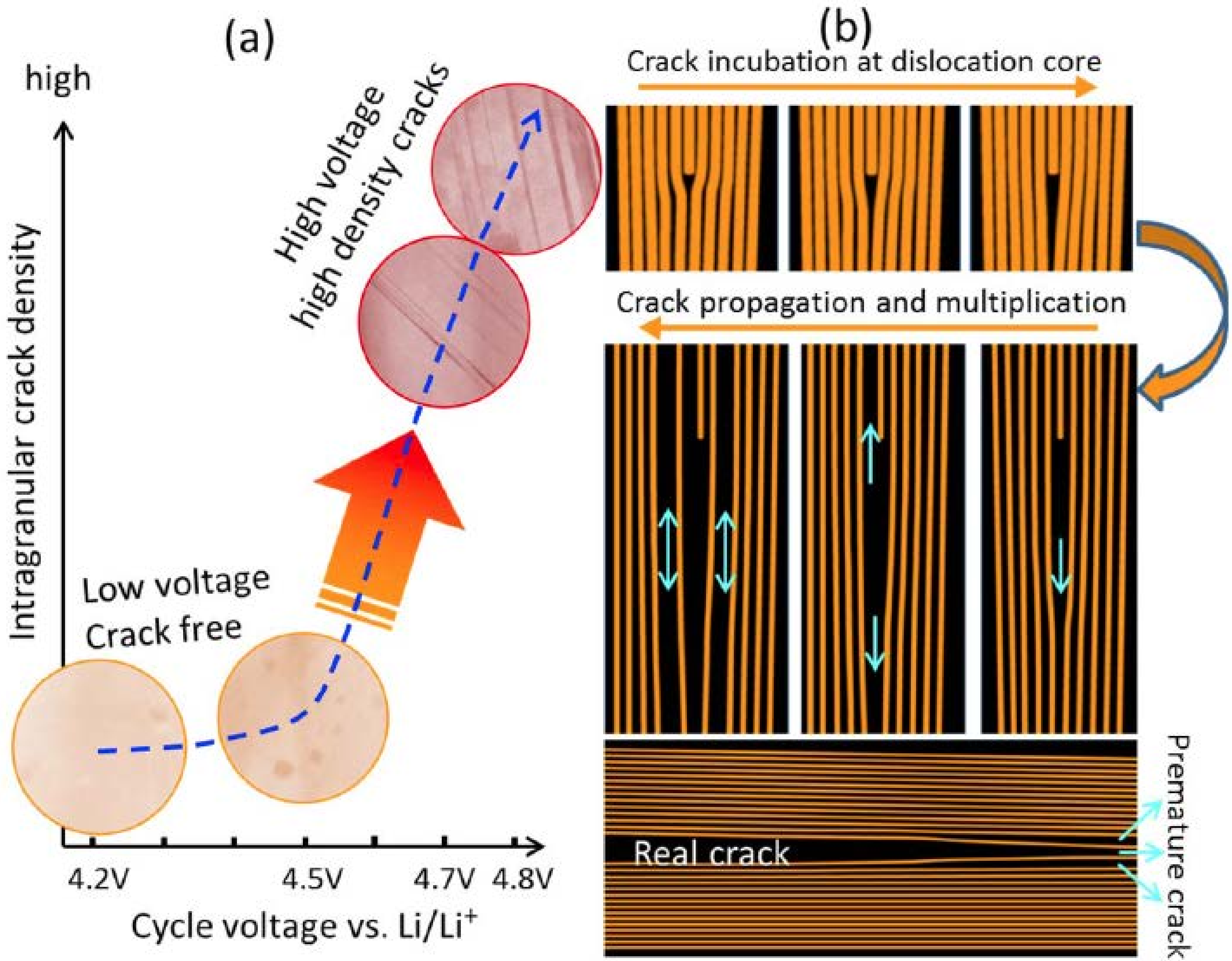
# Technical Accomplishments:

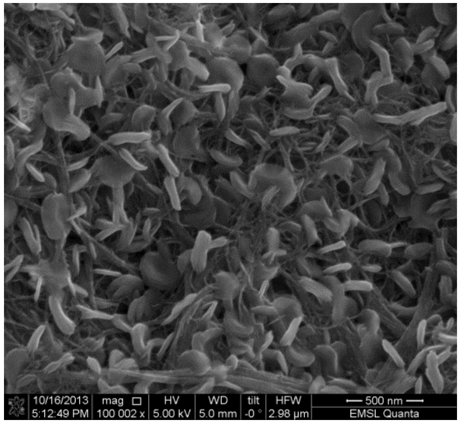
## Dependence of Intragranular Cracks on the Voltage in NMC333

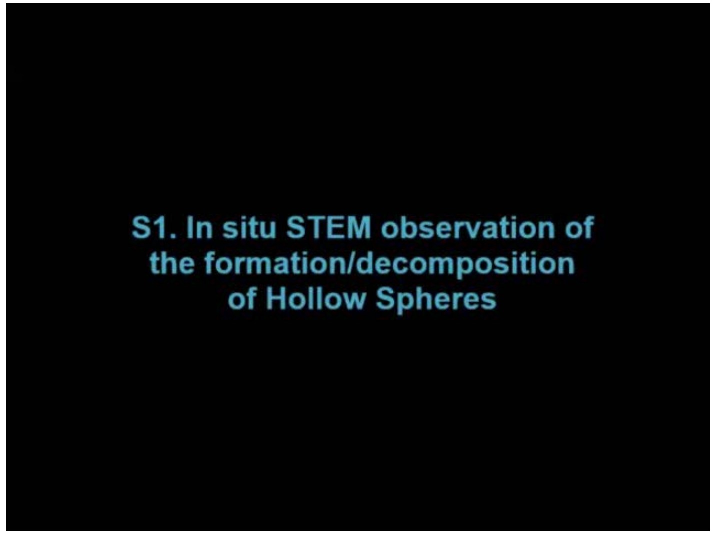


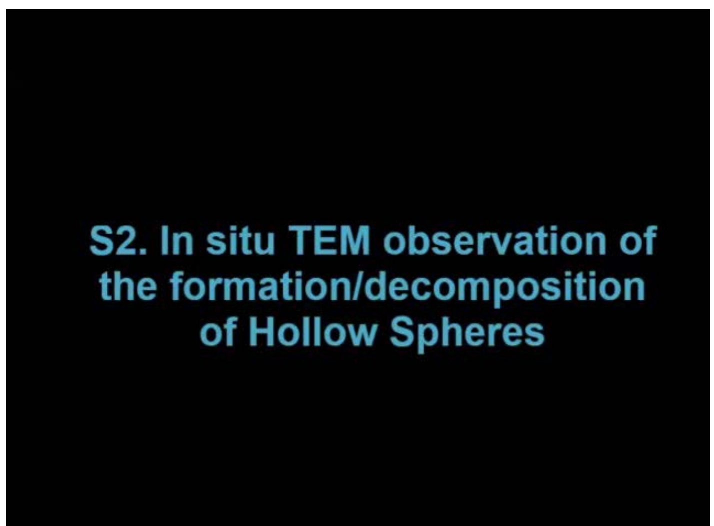

P. F. Yan and C. M. Wang et al.. Nat. Commun.8, 14101 (2017)

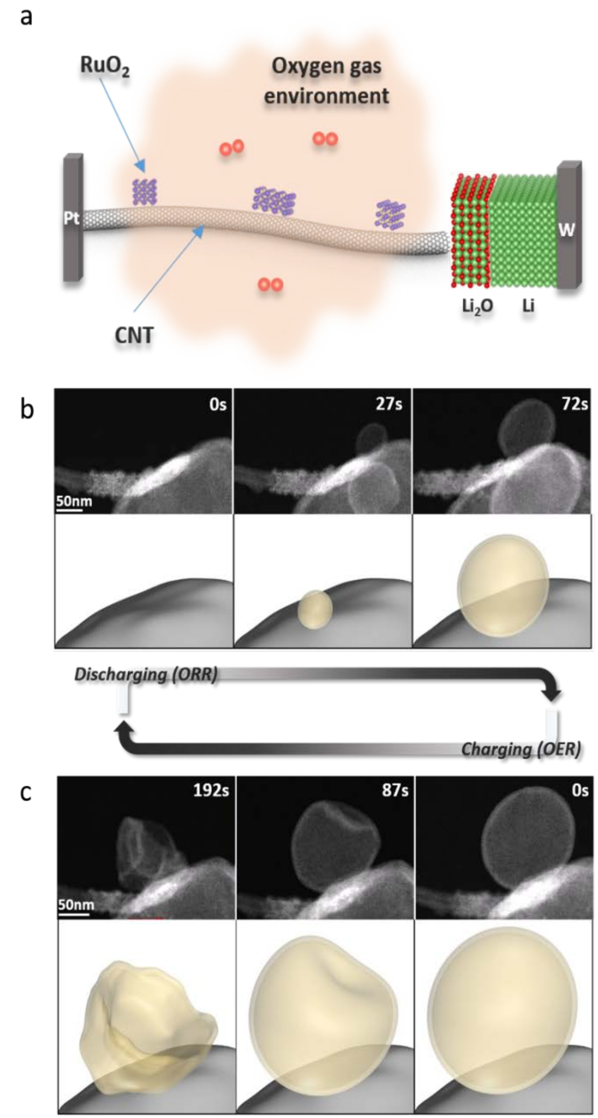
# Technical Accomplishments:

## Revealing the Reaction Mechanism and Mystery of Li-$O_2$ Battery using in-situ ETEM



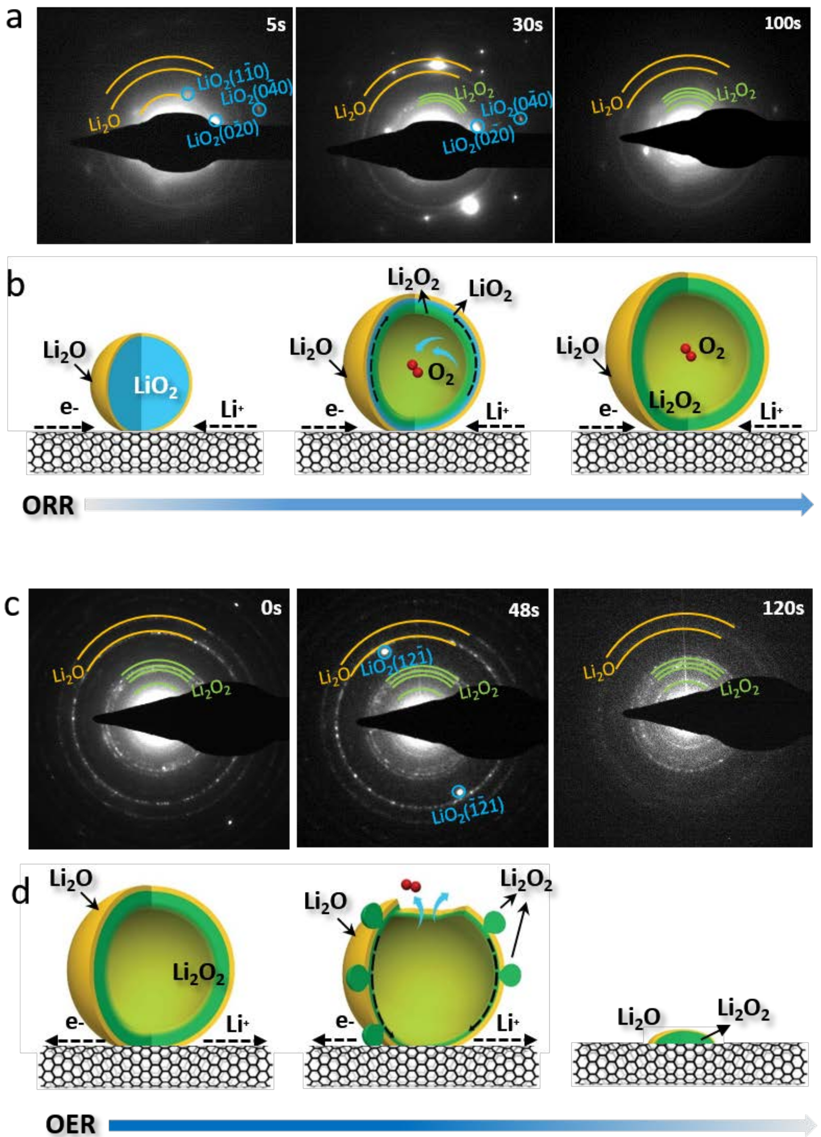

- Morphology of Li-$O_2$ reaction products appear to be complexing
- It remains as a mystery



L. L. Luo and C. M. Wang et al, Nature Nanotechnology, 2017, online

# Technical Accomplishments:

## In Situ Electron Diffraction Analysis of Phase Evolution and Reaction Mechanisms




- Discharging, $LiO_2$ was formed, which subsequently evolves to $Li_2O_2$ and $O_2$ through disproportionation reaction
- $O_2$ gas inflates the particle to a hollow structure
- Charging, $Li_2O_2$ decomposes, leading to the collapse of the hollow spherical particles
- Critical insight as how does the toroidal structure form in Li-$O_2$

L. L. Luo and C. M. Wang et al, Nature Nanotechnology, 2017, online

# Responses to Previous Year Reviewers' Comments

- Made a poster presentation, the project was not reviewed in 2016

# Collaboration and Coordination with Other Institutions

**Partners:**

- Material synthesis group in PNNL: Preparation of both cathode and Si based anode materials
- Argonne National Lab: Preparation of cathode materials, ALD coating
- Lawrence Berkeley National Lab: Preparation of cathode materials
- Stanford University: Si nanowire based anode and surface coating
- GM Research Center: Prepared porous Si, S enclosed in carbon
- National Renewable Energy Lab: ALD coated Si samples
- Hummingbird Scientific: Help to develop the liquid holder
- University of Texas at Austin: Preparation of cathode and anode materials
- FEI Company: ETEM capability development

# Remaining Challenges and Barriers

- For SEI and Li dendrite studies using liquid cell TEM, building of a half cell or a full cell battery is always a challenge. More develop is needed based on deposition or microchip techniques

- Minimizing the liquid layer thickness to gain a better resolution in liquid cell. This can be achieved by designing of the liquid window geometry to minimize the bulging effect

- Capability to measure ultra small current in the liquid cell to enable

- Due to the complicated steps of assembling the in-situ cell, the reliability and reproducibility of the in-situ and operando TEM cell need to be improved

# Proposed Future Work

❖ **FY2017**

- Bulk degradation mechanism of cathode: Vacancy injection and clustering to form void in the bulk lattice
- Continue the study of the fading mechanism of LMR, NMC, and NCA based cathode and correlate with fading mechanism
- Using in-situ TEM to gain atomic view on the intragranular crack formation process

❖ **FY2018**

- Strategy of mitigating the cathode-liquid electrolyte reaction: some new concepts have been demonstrated
- Detailed structure of SEI layers on anode: direct visualization of electrical double layer using in-situ liquid SIMS
- Identification of dopant to stabilize the lattice

Any proposed future work is subject to change based on funding levels

# Summary

- To attack the problem of capacity fading related to cathode, mitigating the solid-liquid electrolyte reaction is a critical step

- For secondary particles, the liquid electrolyte indeed penetrates into the boundaries

- A critical barrier for high voltage application of layer structured cathode is the intragranullar cracking, needs find way to stabilize the lattice, such as doping

- Revealed the mystery of the toroidal morphology of reaction products in Li-$O_2$ battery, providing clues for deciphering the mass/charge transport and $O_2$ releasing process in Li-$O_2$ system

# Technical Back-Up Slides

# Patents/Publications/Presentations

1: Pengfei Yan, Jianming Zheng, Meng Gu, Jie Xiao, Ji-Guang Zhang, Chongmin Wang, "Intragranular cracking as a critical barrier for high-voltage usage of layer-structured cathode for lithium-ion batteries", **Nat. Commun. 8, 14101 (2017).**

2: Langli Luo, Bin Liu, Shidong Song, Wu Xu, Ji-Guang Zhang and Chongmin Wang, "Revealing the reaction mechanisms of Li–O2 batteries using environmental transmission electron microscopy", **Nature Nanotechnology, 2017 online**

2: Pengfei Yan, Jianming Zheng, Xiaofeng Zhang, Rui Xu, Khalil Amine, Jie Xiao, Ji-Guang Zhang, and Chong-Min Wang, "Atomic to Nanoscale Investigation of Functionalities of an $Al_2O_3$ Coating Layer on a Cathode for Enhanced Battery Performance", **Chem. Mater., 28, 857−863 (2016).**

3: Yang He, Meng Gu, Haiyan Xiao, Langli Luo, Yuyan Shao, Fei Gao, Yingge Du, Scott X. Mao, and Chongmin Wang, "Atomistic Conversion Reaction Mechanism of $WO_3$ in Secondary Ion Batteries of Li, Na, and Ca", **Angew. Chem. Int. Ed. 55, 6244 –6247 (2016).**

4: Pengfei Yan, Jianming Zheng, Jiaxin Zheng, Zhiguo Wang, Gaofeng Teng, Saravanan Kuppan, Jie Xiao, Guoying Chen, Feng Pan, Ji-Guang Zhang, and Chong-Min Wang, "Ni and Co Segregations on Selective Surface Facetsand Rational Design of Layered Lithium Transition-Metal Oxide Cathodes", **Adv. Energy Mater. 6, 1502455 (2016).**

5: Zhaofeng Gan, Meng Gu, Jianshi Tang, Chiu-Yen Wang,Yang He, Kang L. Wang, Chongmin Wang, David J. Smith, and Martha R. McCartney, "Direct Mapping of Charge Distribution during Lithiation of Ge Nanowires Using Off-Axis Electron Holography", **Nano Lett. 16, 3748−3753 (2016)**

6: Jiangwei Wang, Hao Luo, Yang Liu, Yang He, Feifei Fan, Ze Zhang, Scott X. Mao, Chongmin Wang, and Ting Zhu, "Tuning the Outward to Inward Swelling in Lithiated Silicon Nanotubes via Surface Oxide Coating", **Nano Lett. 2016, 16, 5815−5822 (2016).**

7: Chenfei Shen, Mingyuan Ge, Langli Luo, Xin Fang, Yihang Liu, Anyi Zhang, Jiepeng Rong, Chongmin Wang and Chongwu Zhou, "*In Situ* and *Ex Situ* TEM Study of Lithiation Behaviors of Porous Silicon Nanostructures", **Sci. Rep. 6, 31334 (2016).**

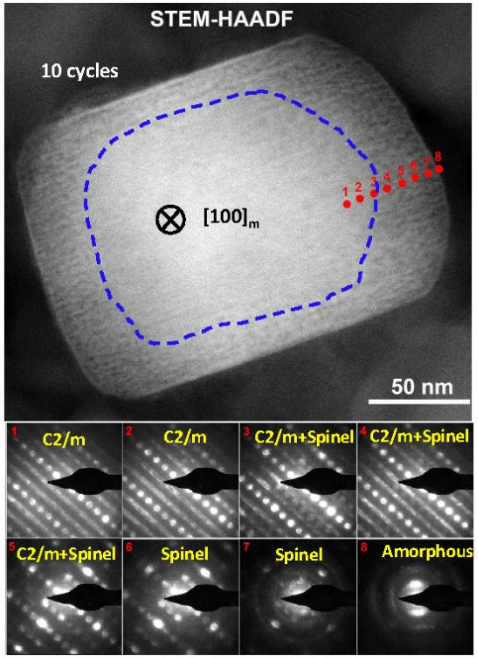
8: Eungje Lee, Joel Blauwkamp, Fernando C. Castro, Jinsong Wu, Vinayak P. Dravid, Pengfei Yan, Chongmin Wang, Soo Kim, Christopher Wolverton, Roy Benedek, Fulya Dogan, Joong Sun Park, Jason R. Croy, and Michael M. Thackeray, "Exploring Lithium-Cobalt-Nickel Oxide Spinel Electrodes for ≥3.5 V Li-Ion Cells", **ACS Appl. Mater. Interfaces, 8, 27720-27729(2016).**

# Acknowledgements

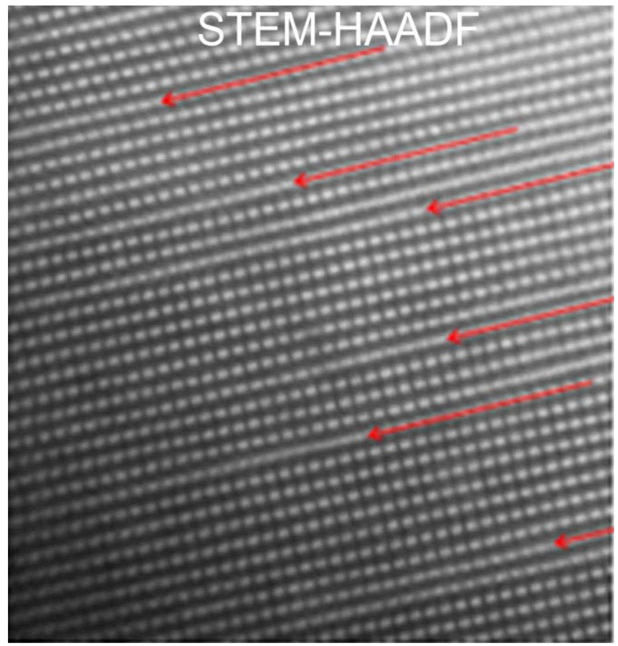

- ✓ Supports from the U.S. Department of Energy, Office of Vehicle Technologies Program are gratefully appreciated.

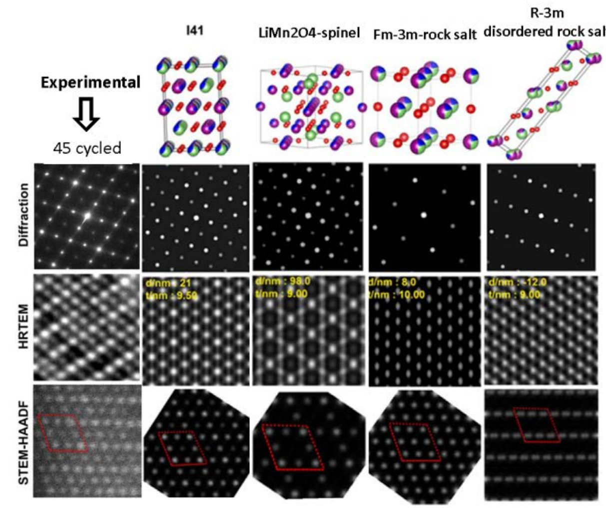
- ✓ Team Members:
  Pengfei Yan, Langli Luo, Jianming Zheng, Wu Xu, Xiaolin Li, Jie Xiao, Jun Liu, and Ji-Guang Zhang

# The Structure Change Route of $Li_2MnO_3$ Synthesized by CP Method




8-position line scan of a 10-cycles sample using nano beam electron diffraction. The crystal orientation can be assigned to [100] for C2/m structure and [112] for spinel structure.




Comparison between experimental results and simulation results of different crystal models for the SRL from the [010] zone axis. I41 structure matches best in the four crystal models.